

Self-organization of highly ordered mosaic structure of porous silicon at long anodic etching of p-type Si in the electrolyte with internal source of current

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Abstracts-- Self-organization of highly ordered mosaic structure of porous Si at long anodic etching of p-Si (100) in electrolyte with internal source of current is observed. Sizes of the nanocrystallites islets of porous Si, the period of their location and self-organization of the mosaic structure of porous silicon are defined by the effects of forces of elastically-deformation, defect-deformation and capillary-fluctuation, which exist at the interface of electrolyte/porous Si/c-Si/ in process of pores formation. Process of spontaneous formation of mosaic structure por-Si has place in result of the relaxation of elastically-strained layer of porous surface and the influence of capillary-fluctuation forces. Shown is a substantial role of the oxidized silicon surface during the formation of islets of the mosaic structure por-Si during long anodic etching p-Si (100) in the electrolyte HF: H₂O₂. The main features of formation and ordering of three-dimensional islets of nanocrystallites por-Si during long anodic etching are discussed. Formation and ordering of them occurs due to quantum size effects, taking place on the local microscopic the sites of atomically rough surface of real crystal Si as well as in the case of epitaxial growth of nanocrystallites and their self-assembled on the surface of semiconductors A₃B₅ and Si. Conditions of development of these forces depend from the self-coordinated parameters of etching interface the electrolyte/porous Si/c-Si/ and parameters of electrodes and the electrochemical cell. Based on the results of the processes of pore formation in the monocrystal of silicon at etching his and further formation of cracks at long etching is made conclusion about the common nature of cracks of radiation and nonradiation the origin in the conditions of soft influence when possible formation of quasi-equilibrium point defects and their subsequent migration to the different drains.

Keywords: self-organization, mosaic structure, surface, interface, porous Si, electrolyte, nanocrystallites, cracks, point defects, soft influence. monocrystal.

I. Introduction

Earlier [1] at long anodic etching p-Si (100) in the electrolytes with internal source of current, when the system of hydrofluoric acid and ethanol has the addition of hydrogen peroxide, the spontaneous formation of highly ordered mosaic structure (MS) of the surface of porous silicon (por-Si) is observed (Fig. 1 [2]). MS por-Si is formed in view the array of islets from oxidized

nanocrystallites (NCs) with diameters between 10 and 20 nm [3], separated by silicon ledges.

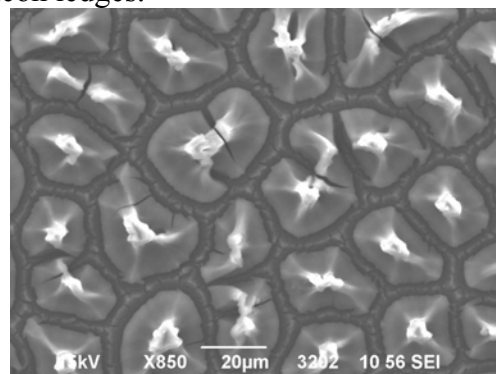


Fig.1. SEM micrograph of surface por-Si [2]. The electrolyte—HF (49%):H₂O₂ (40%) = 1:1, t_{etch.} = 240 min.

The spectrum of photoluminescence (PhL) of these por-Si samples shown is (fig. 2) in the interval of wavelength $\lambda = 340-800$ nm with maximum intensities at $\lambda = 640$ nm, which shifted to long-wave wing of spectrum, to higher energies, in comparison with spectra PhL of por-Si samples, the received in standard HF-electrolyte without H₂O₂. This indicates on the formation of predominant of nano-sized silicon crystallites in these samples. Formation of MS por-Si on Si surface with plane (100) at long anodic etching is preceded the formation of secondary layer from Si

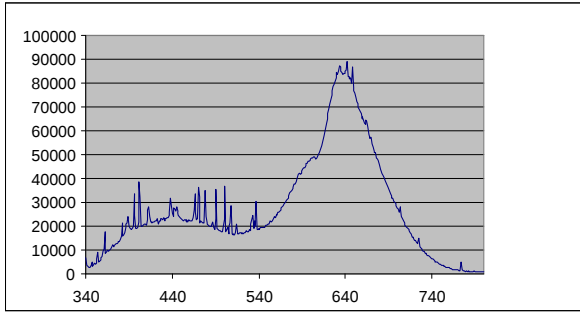


Fig.2. The spectrum of photoluminescence of samples por-Si, after etching in electrolyte HF (49%):H₂O₂ (40%), $t_{\text{etch.}} = 240$ min. He-Cd laser, $\lambda_{\text{exc}} = 325$ nm.

atoms adsorbed (adatoms Si) by pores, which are besieged on por-Si surface [3].

At the achievement of certain thickness ($d_{\text{por}} = 20 \mu\text{m}$) on this layer are formed of cracks in form netted texture of surface with certain crystallographic orientation. Formation of netted texture on surface of thin film of secondary layer of Si adatoms occurs because of relaxation of elastically strained layer, i.e. morphological instability of the strained layer is observed [4].

The netted texture of secondary's layer of NCs por-Si at the further etching is transformed to islets formations of the certain form and sizes, and the certain periodicity of localization. Highly ordered MS surface of por-Si is formed (fig.1).

This article considers the formation mechanism of highly ordered MS por-Si at long anodic etching in electrolyte with internal source of current.

II. Experimental details and results

Samples Si (B), $\rho=0.01 \Omega\cdot\text{cm}$ and with plane of crystallographic orientation (100) (series 1) and Si (B), $\rho=10 \Omega\cdot\text{cm}$ with plane of crystallographic orientation (111) (series 2) were used. Ohmic In-contacts were created on the back side of the samples by annealing at 300°C during 30 min. Anode was p-Si, cathode - Ni. Etching was carried out in the electrolyte HF (49 %): H₂O₂ (40 %) = 1:1. The densities of anodic current were $j_a = 3.0 \text{ mA/cm}^2$ for series 1, and $j_a = 0.5 \text{ mA/cm}^2$ for series 2 at the identical parameters of etching and electrochemical cell. The porous surfaces of silicon were researched by the scanning electron (JSM-6490LA) and atomic force (JSPM5200) microscopes.

At long ($t_{\text{etch.}} = 240$ min) etching of p-Si (100) in electrolyte HF: H₂O₂, the self-formation of MS por-Si surface with high degree of ordering of array three-dimensional islets of NCs por-Si is observed (fig.3).

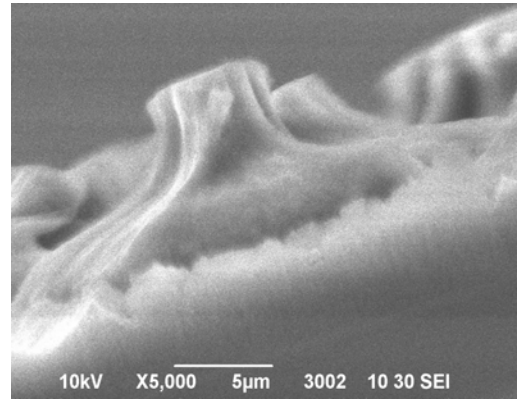


Fig.3. Cross sectional SEM micrograph of por-Si shown on fig.1.

Structure of pores has the regular form of threadlike NCs por-Si, oriented along cubic axis $\langle 100 \rangle$ and at long etching is transformed in array of islets NCs por-Si.

Formation of highly ordered MS por-Si surface is observed at electrochemical etching of p-Si (100) only in HF: H₂O₂ when in electrolyte there is the strong oxidizing agent H₂O₂. Similar etching of p-Si (100) in standard electrolytes (HF: H₂O or HF: H₂O: C₂H₅OH) with external source of current does not lead to formation of highly ordered MS por-Si surface.

In experiments at long etching ($t_{\text{etch.}} = 240$ min and more) of samples p-Si with plane of crystallographic orientation (111) in electrolyte HF: H₂O₂ the MS por-Si is not formed [1, 3]. The homogeneous nanopores in p-Si (111) are formed, which have form of corals (fig. 4), unlike the threadlike structure of pores on surface Si (100).

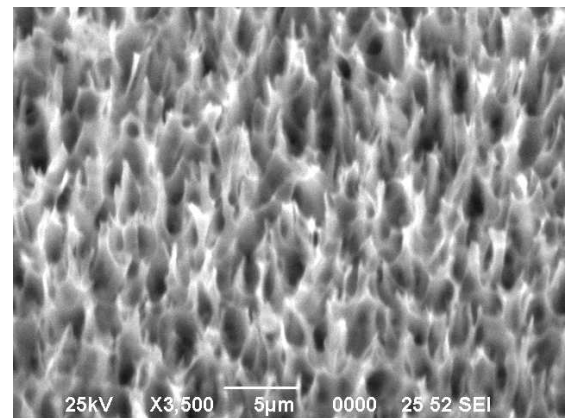


Fig.4. SEM micrograph of surface por-Si. Sample p-Si (111), electrolyte—HF (49%):H₂O₂ (40%) = 1:1, $t_{\text{etch.}} = 300$ min

At the long ($t_{\text{etch}} = 240$ min) etching of p -Si (100) planes, self-organization of por-Si with a high degree of arrangement islets is observed (Fig. 5).

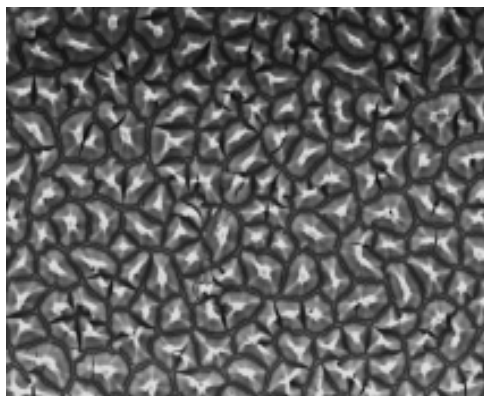


Fig.5. Electron-microscopy images of the mosaic structure por-Si after etching in the HF (49 wt %): H_2O_2 (40 wt %) electrolyte for time $t_{\text{etch}} = 240$ min [3].

On the figure 6 shown the quantitative analysis of the distribution of sizes islets NCs por-Si, showing on the fig.5. Seen, that their average diameter is $\sim 18 \mu\text{m}$, although the sizes of some islets are distinct, which is explained by the features of electrochemical etching.

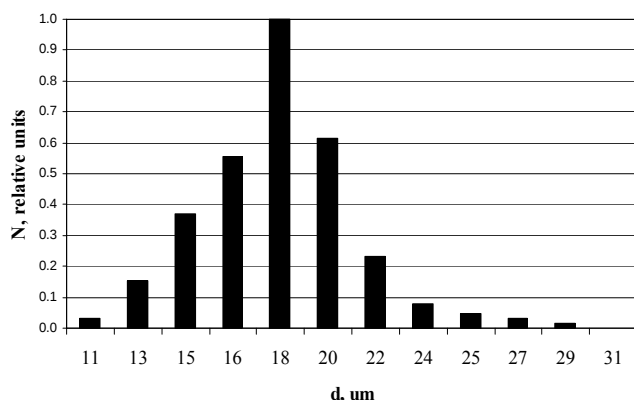


Fig. 6. Histogram of the size distributions diameters islets oxidized por-Si nanocrystallites.

The elemental analysis of islets, of ledges and bottoms of free cells shown (fig.7), that islets represent clusters of oxidized silicon nanocrystallites; cells (bottoms) and ledges consist from Si [1].

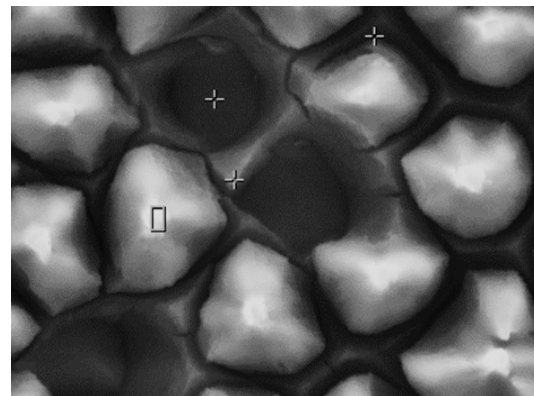


Fig. 7. SEM micrograph [1] of surface of area formed islands of por-Si and elemental composition of its separate parts after annealing at 300°C : 001—the island with elemental composition of 30 at % Si, 51.81 at % O, 17.65 at % C; 002—the resting track of island, 50.17 at % Si, 35.09 at % O, 14.75 at % C; 003—bottom of cell, 66.64 at % Si, 33.36 at % O, C is absent; 004—the ledge_dimple, 88.45 at % Si, 11.55 at % O, C is absent. The composition of electrolyte—HF (49%): H_2O_2 (40%): $\text{H}_2\text{C}_5\text{OH} = 1:1:1$.

The origination of such a MS por-Si from the individual nanocrystallite islets is preceded by the formation of homogeneous nanoporous layers with thickness $d_{\text{por}} = 1, 2, 4, 7, 18, 20 \mu\text{m}$ at etching times $t_{\text{etch}} = 1, 2, 5, 15, 30, 45$ min, respectively. At etching 45 min and longer, the thickness of nanoporous layer remains unchanged ($20 \mu\text{m}$). Figure 8 shows the atomic-force images of the surface por-Si after etching of c -Si for 30 min on which can see uniformly distributed nanopores ~ 10 nm in diameter.

At the long anodic etching the electrolyte solution saturates by atoms Si, which formed in the results of reaction

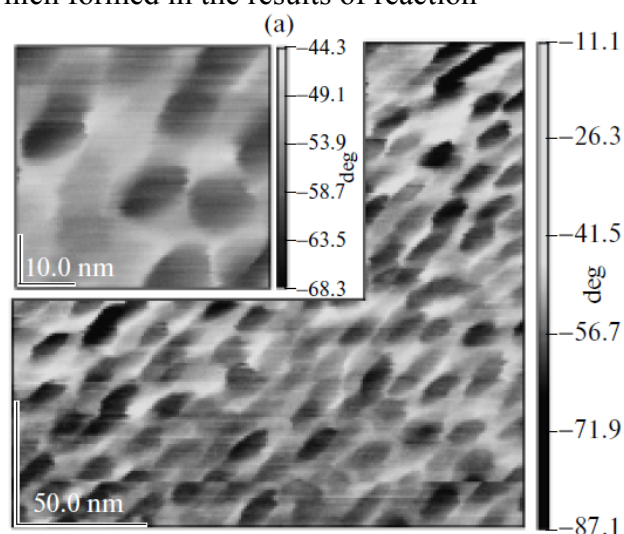


Fig.8. Atomic-force image of the topography of the porous silicon surfaces 200×200 nm and 50×50 nm after etching of p -Si (100) in the electrolyte HF (49 wt %) : H_2O_2 (40 wt %), $t_{\text{etch}} = 30$ min.

autodisproportionation [5] and on the surface of por-Si formed the secondary porous layer consisting of phases amorphization and recrystallization [7]. The surface of aggregates of adatoms Si usually covered by the complexes compounds of reaction products of anodizing, adsorption from the environment, including oxides of silicon.

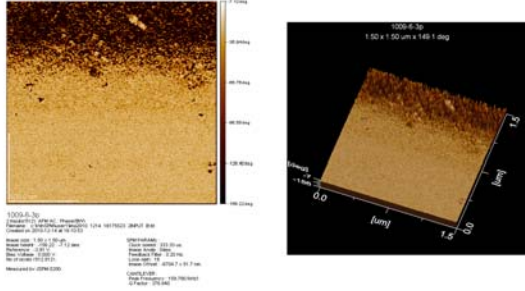


Fig.9. Atomic-force images of the porous silicon surfaces 1500 x 1500 nm, the topography (a) and phase contrast (b), after etching in the electrolyte HF (49 wt %) : H₂O₂ (40 wt %), $t_{\text{etch}} = 60$ min.

On the fig.9 are observed two sites of the porous layer from of deposited silicon atoms and silicon nanocrystallites of por-Si. The thickness of secondary porous layer of NCs por-Si is $d_{\text{por}} = 20$ μm .

At $t_{\text{etch}} = 60$ min and more on the surface por-Si appears the texture netted (Fig. 10), which is formed by cracks in the porous layer.

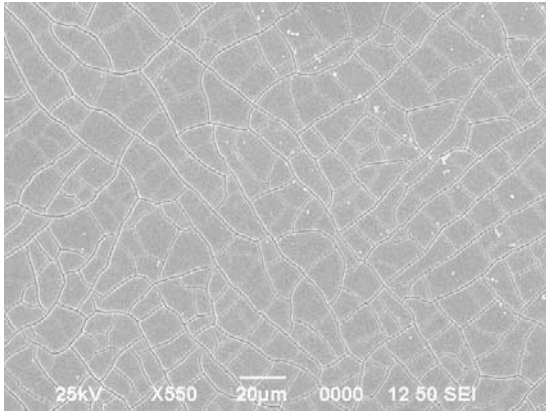


Fig. 10. Electron-microscopy image the netted texture of cracks on the surface p-Si (100) sample after etch $t_{\text{etch}} = 60$ min.

During further etching ($t_{\text{etch}} = 120$ min and longer) the texture netted on the por-Si surface is transformed to the mosaic structure (Fig. 1).

The formation of netted texture occurs, mainly, as a result of morphological instability of strained secondary layer NCs por-Si in the process of his relaxation under the influence of elastic deformation forces due to the mismatch of lattice

parameters [4] films por-Si and Si-substrate. At the achievement of critical elastic strain corresponding to the critical thickness of the surface defect layer (porous layer $d_{\text{por}} = 20$ μm), this elastically strained layer is relaxed by formation of cracking on the surface of secondary layer NCs por-Si.

III. Discussion

Formation of such high degree of MS por-Si surface (fig. 1) is observed for the first time [1], though there are the works (see [5, 8] and references there) in which the formation of MS por-Si surface is observed, but the morphology of por-Si surface does not have so high degree of mosaic structure, as in our case. Similar structures was observed, when por-Si dries with water, and authors considered, that the formation of pseudo-mosaic structure is related with the mechanical strain, arising at the drying of por-Si, that leads to surface cracking, as result of impact of tension forces [8]. Formation of highly ordered MS por-Si surface during the electrochemical etching of p-Si (100) only in HF: H₂O₂, when the electrolyte has strong oxidizing agent H₂O₂, indicates a crucial role of surface oxidation at the formation of MS por-Si. We consider that formation of MS por-Si occurs also, as well as in case of growth NCs-Si with the smallest sizes (< 10 nm) and highest density ($10^{12} - 10^{13}$ cm⁻²) on the oxidized surface of Si at the epitaxial growth of islets NCs-Si on Si matrix, when the mechanism of nucleation of islets NCs-Si consists from direct interaction of besieged Si atoms with atomic-pure Si surface as a result of desorption of oxygen atoms [9]. At this, the role of mechanical strain because of discrepancy of parameters of NCs por-Si and Si lattices ignored. As shown [10], at the addition of H₂O₂ in HF-electrolyte, the NCs por-Si are formed with the small sizes, smaller dispersion and with smaller thickness of porous layer, than pores at the formation in standard electrolyte without H₂O₂. Authors supposed that it is related with more intensive oxidizing of surface NCs of por-Si because of

presence in electrolyte of strong the oxidizing agent, which is formed at the formation of pores in HF-electrolyte with H_2O_2 . The role of strong an oxidizing agent in this case plays the singlet oxygen that formed in the presence of dissolved oxygen in such electrolyte under illumination of NCs- Si [11]. We also do not exclude the role of singlet oxygen in the formation process of MS por-Si at long etching of p-Si (100) in HF: H_2O_2 , which are formed in the electrolyte HF with the addition of H_2O_2 through the catalytic effect of the developed surface of por-Si.

Formation of MS por-Si on the c-Si with plane (100) and absence of MS on Si (111) at the same conditions of etching indicates on difference of speed of electrochemical etching of Si surface, which is maximal in direction [100]. The large speed of etching of plane Si (100) determines by smaller number of Si atoms, which participate in formation of array of NCs por-Si islets on Si surface with plane (100), and according to [12] determines both shape and sizes of islets. Moreover, the growth facets of Si atoms surface on crystallographic direction [111] has a large energy, than for atoms Si in the plane (100), and atomic smoothness of surface (111) more than comparison with (100), i.e. this facets have the large morphological stability [13]. And this is the main reason that the MS of por-Si on Si (111) at the long process of electrochemical etching is not formed due to high energy of formation of steps and kinks on atomic - rough plane (111) compared to the (100). As well known [4, 9, 12, 13], surface Si (100) is most optimum for epitaxial formation coherent nanoislets. Formation of three-dimensional islets of por-Si by transformation of the secondary layer from adatoms Si occurs similarly as transformation at epitaxial grow of layers thin film to formations of three-dimensional NCs-Si islets in result of action of forces of elastic strain and the surface tension [4, 12 and 13]. The basic centers of origin of NCs-Si islets are determined by balance of surface energies of film and substrate, and also by energy interface of film-substrate and the internal energy of volume islet. The main factor of islets growth is energy gain because of the diminish of strain in layers thin film with help by their elastic relaxation when the energy of rough surface of strained layer becomes less than the sum energies from energy of strain in volume of the islets and the surface energy in tops of the islets [4]. Formation of 3D islets NCs por-Si at long etching also occurs due

to the energy gain in the formation of 3D islets in the form of truncated pyramids (fig. 3). Such shape of islets corresponds to minimum energy of formation of islets on Si (100) surfaces of elastically-anisotropic cubic crystal [4]. Although there are also other shapes of islets, in particular, quasi-hexagonal, this appears because of by features of the process of electrochemical etching process in isotropic liquid medium, where the minimum energy of islets should correspond to hexagonal form of the islets. Formation of islets NCs por-Si is result of the morphological instability of strained films because of the actions of elastic deformation forces at mismatch of lattice parameters of the film por-Si and Si-substrate [4], and of the defect-deformation forces [14] emerging in process spatial-temporal ordering I_{Si} and V_{Si} , of products elementary acts of reactions of silicon etching.

The analysis of the dynamics the formation cracks, the islands and ledges shows (fig. 1) that the formation cracks on surface the por-Si is based on originated the silicon of ledges. Silicon ledges are formed on the c-Si surface under the por-Si layer from the material of the Si-substrate during its etching.

For determination the mechanism of MS por-Si and the nature of the formation of cracks on the surface of porous silicon investigated of the electron- microscopic images of the porous surface at different time of anodic etching. With this aim was studied of electron microscopic images of the surface of por-Si for samples prepared at etching of 60–240 min. The time of etching is caused by the fact that the por-Si surface is transformed in this range of etching from the formation cracking and netted texture to the MS of por-Si.

Figure 11 shows the electron-microscopic images of the surface area of the por-Si sample after etching for a time $t_{\text{etch}} = 120$ min, in which we can see surface with different degrees of etching due to nonuniformity etch [5]. In the central sample region the etch rate is higher than at the periphery. The

nonuniformity of etching of the sample surface allows all main stages of the formation of the MS por-Si. On the peripheral sample region occurs the formation of initial stage of quasiparallel of cracks because of the lower etch rate, and they

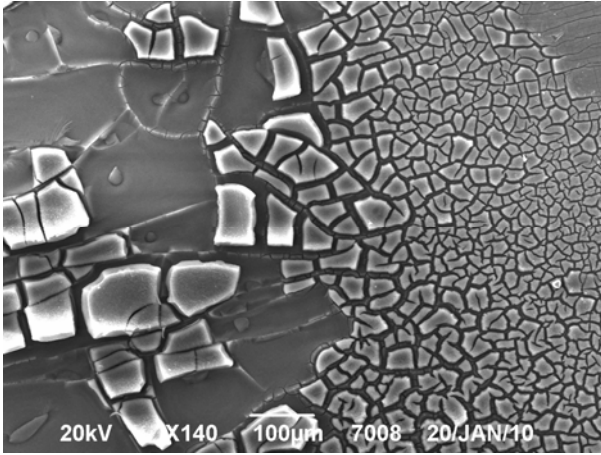


Fig. 11. Electron-microscopy images of the silicon sample surface at the etching time $t_{\text{etch}} = 120$ min [3].

are arranged at the distance of $\sim 20 \mu\text{m}$ from each other along the crystallographic direction [010] (fig. 12). Closer to the sample center, i.e., where the efficiency of etching increases, these cracks [010] are intersected with transverse cracks along the [001] axis, the also arranged practically at the same distance from each other. The origination of transverse [001] cracks after [010] crack formation is caused by the cubic lattice of silicon and increase elastic deformation forces of the surface [4, 14] at increase thickness of the porous layer. Further development of these cracks ([010], [001]) results to formation of netted texture. In central region of sample partially formed MS por-Si as flat irregular regions, separated by ledges. In some areas have free cells from remote por-Si islets, which makes possible to clearly observe, how the formed islands and cells, framed by ledges.

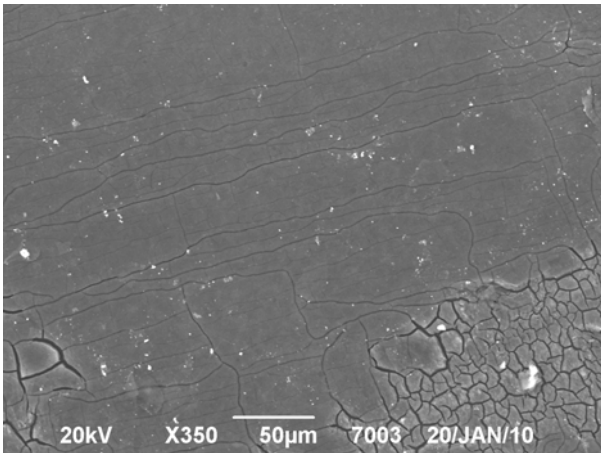


Fig. 12. Electron-microscopy images of the quasi-parallel cracks on the porous silicon sample surface, $t_{\text{etch}} = 120$ min [3].

To explain the dynamics of the origination and formation of silicon ledges, we used the model of the defect deformation mechanism (DDM) of ordering of point defects (PDs), i.e., interstitials I_{Si} and vacancies V_{Si} produced during silicon etching reaction [14]. It should be taken into account that products of etching reactions I_{Si} and V_{Si} simultaneously are structural defects in surface regions of *c*-Si. I_{Si} , due to their high mobility, are moved rapidly than V_{Si} to of the different drains and for long distances. In the case of por-Si the drains for I_{Si} are the interfaces of NCs por-Si/*c*-Si of the elastically-strained layer due to mismatch of the lattice parameter between NCs por-Si and *c*-Si, since NCs por-Si represent an inhomogeneous system of *c*-Si coated with layers of its hydrides and oxides [5-7]. Preferred directions motions of I_{Si} are the crystallographic axes with the least of density of lattice atom packing [4]. For surface the plane of *c*-Si (100) these are [010] and [001] directions. Also V_{Si} are moved to the different drains, however, their diffusion rate is low in comparison with I_{Si} . Therefore, V_{Si} , as a rule, are concentrated on the *c*-Si surface, being centers of pore nucleation [14]. Thus, the spatio-temporal distribution of I_{Si} and V_{Si} is formed, and they are localized in the *c*-Si surface region, which results in the formation of a wave relief of surface, as ledges and valleys, and additional deformation of the crystal surface. At the achievement of critical threshold the concentrations of I_{Si} and V_{Si} occurs their spontaneous self-ordering. V_{Si} are self-ordered uniformly over the surface as quasihexagonal structures [14]; I_{Si} are self-ordered mostly along [010] and [001] crystallographic orientations at the NCs por-Si/*c*-Si interface. I_{Si} clustering results in the origination of silicon ledges under of the elastically-strained porous layer at the interface of NCs por-Si/*c*-Si. At grows of ledges, their stress on the

porous layer of silicon increases. At the achievement of the critical elastic strain corresponding to the critical thickness of the surface defect layer (porous layer d_{por}), this elastically-strained layer [4] is relaxed by cracking on the por-Si surface along [010] and [001] directions.

Also are observed cracks on the silicon ledges of the MS por-Si, which have characteristic direction, caused by the crystallographic of orientation of the substrate material (fig.13).

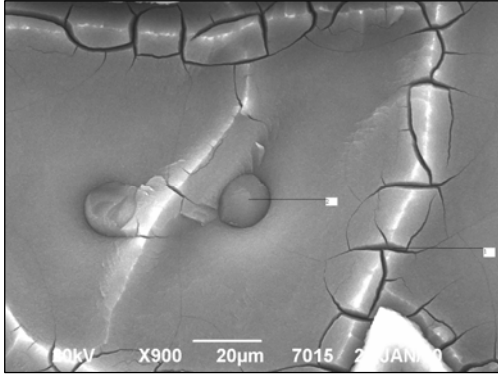


Fig. 13. Electron microscopy images of the cracks on the silicon ledges of porous silicon sample surface, $t_{\text{etch}} = 120$ min.

The cracks are formed on silicon ledges due to the accumulation of I_{Si} in the interstitial space of the crystal lattice of silicon in the surface region because the formation of the mosaic structure of the por-Si surface has a fractal nature (fig.14).

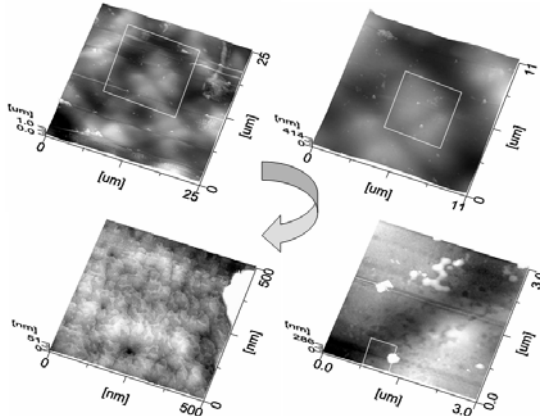


Fig. 14. Atomic-force images surface of the islets of NCs por-Si at different magnifications, $t_{\text{etch}} = 120$ min. The scale magnification direction is indicated by arrow.

Figure 14 is a fragment of topography region surface of porous silicon on the ledge (fig. 13) at the different scales of magnification. It is seen that the surface relief of por-Si repeats and is characterized by the hillocks and the valleys, on which NCs por-Si in the form of dendritic formations are arranged. However, unlike the data

[5,7], where previously the nanoparticle fractals the sizes 10–100 nm were observed, in our the case, islands of oxidized NCs por-Si have sizes 18–20 μm and are also fractals. According to [5] can assume that the fractal nature of the formation mechanism of the mosaic structure is caused by fluctuations of the electric field at the electrolyte/ NCs por-Si /c-Si/ interface [15] due to the highly developed por-Si surface. Due to fluctuations of the electric field at the interface electrolyte/ NCs por-Si /c-Si and due to other additional conditions [16], which are given below, appears regions charge localization, where etching of the surface with formation of mosaic structure is more intensive.

Fundamental importance has the solution of problem of distance between cracks that eventually defines the period of MS por-Si. The distance between the cracks and between the islets of MS por-Si are determined by the combined effects of elastic deformation forces [4], DDM [14], and mainly the fluctuation-capillary forces, that arise in thin submicron layer of charged liquid (electrolyte) on the electrode surface [15, 16], which arises at passing electric current on interface electrolyte/NCs por-Si/c-Si. Period of wave vibrations capillary-fluctuation forces, depending on the defect layer thickness, can also reach significant values (micrometers and larger). As result this are formed the of submicrometer sizes of three-dimensional islets of oxidized NCs por-Si [3].

Earlier [15] were shown instability the plane profile of interface silicon/electrolyte during the anodic etching of n-type silicon. Instability of the flat profile of por-Si was associated with small perturbations at the interface of electrolyte/semiconductor caused by transport of holes in silicon and ions in electrolyte, and by the surface energy of the capillary tension of silicon [17], on analogy with morphological of the instability that occurs at the nucleation of crystal growth [18]. There assumed, that the wavelength of the perturbation determines the order of the distances (100

- 1000nm) between the pores in silicon n-type. However, the results arising from [15], not confirmed results for the distances between the pores in p-type silicon, where sizes interporous distance were small (1-10nm).

Nevertheless, by analogy with [15] and with the involvement of the additional results of works [16, 19, 20], we believe, that the of capillary-fluctuation forces, arising on interface electrolyte/por-Si/c-Si/, are responsible for self-organization of MS por-Si at long anodic etching.

Totality of local electrical and thermal fluctuations that occur in microscopic sites of the surface of interface electrolyte/silicon at electrolysis is caused the fluctuations of the local coefficients of surface capillary tension of the layer liquid with the surfaces of por-Si and c-Si. This leads to occurrence of capillary-fluctuation forces, which participate to formation of highly ordered MS por-Si. Under activity of the capillary-fluctuation forces on the surface of thin layer liquid are formed the periodic oscillations of capillary waves [16, 19], influence of which gives process formation of MS por-Si and their self-organization. In the strongly charged the surface layer of electroconductive liquid, what is electrolyte, the distribution of electrical wave has the resonant character, depending on the physico-chemical properties of liquid, values of dielectric inductivity and coefficient of surface tension [19]. The effect exponential increase the vibration amplitude of capillary waves on interface mediums is observed at diminishing of surface tension coefficient of liquid. Presence of periodic electric field of perpendicular to the interface electrolyte/semiconductor leads to magnification with growth of field gradient of values of surface tension coefficient of liquid [16] and, accordingly, to increase of oscillations period of waves at the diminishing of amplitude its oscillations. With increase of inductivity local region of interface the standing of the resonance is moved to region of liquid with small values of surface tension coefficient, that causes the decrease in surface charge density and, accordingly, the decrease speed of etching there. At diminishing of inductivity of local region of interface, the resonance moves to region of liquid with large values of surface tension coefficient that leads to the large local density of surface charges and to increase of the rate local etching of surface of por-Si. Under activity of capillary-fluctuation forces of the interface the electrolyte/semiconductor

arises homogeneous in all surface, but the no homogeneous on amplitude of oscillations, periodic potential of electric field, which defines the formation of MS por-Si surface. Periodic change of the surface capillary forces at the interface of silicon/electrolyte leads to the periodic etching of planar structure of the porous layer. At the minimum of the electrical potential arise islets of NCs por-Si, which divided by dimples and the ledges on silicon matrix, that are formed in places of maximum peak of electrical potential. The period of oscillations of electrical potential in such system depends on thickness of layer strain and can reach hundreds micron [20]. Apparently, the given effect is observed in our experiment at formation MS por-Si, when predominant etching of the local sites and created the MS por-Si. Period of arrangement of MS por-Si islets is located in range of change of periodic potential the electric field under influence of capillary-fluctuation forces. The dominant mechanism of self-organization MS por-Si at long of the anodic etching of p-Si (100) is the mechanism of the capillary-fluctuation forces, arising in thin layer surface of liquid on the interface - electrolyte/por-Si/c-Si.

Finally, the formation cracks and subsequent formation of highly ordered mosaic structure of the porous silicon is observed during long anodic etching in the electrolyte only with an internal current source, when there is self-setting regime of soft etching. Under these conditions, the possible formation of point defects by breaking chemical bonds of atoms in a crystal, their removal from the lattice sites in the interstices and the possible to further migration their to the different drains. And possible their the spatial-temporally of ordering, and the realization of the above mentioned mechanisms of ordering of defects, formation of cracks and formation of highly ordered MS por-Si. These conditions are not always fulfilled, including, and conditions of etching with an external current source when there is a process formation of non-equilibrium

point defects. But when conditions are fulfilled the of soft influence on the crystal, there is formation of quasi-equilibrium point defects and possibly their migration to different drains (for example, the interface of NCs por-Si/c-Si in the case of porous silicon), it may to create cracks and in the further to form of highly ordered the mosaic structure of the crystal surface. Conditions of soft influence on the crystal and the formation of quasi-equilibrium point defects are possible at the near-threshold low-energy effects by laser, ion implantation, the thermal and mechanical influences, etc. Formation of highly ordered MS on surfaces of metal, insulators and semiconductors (e.g., Al, Al₂O₃, GaAs) are observed at low-energy laser, ion, and electronic effects, at the mechanical strain [14 and references there].

IV. Conclusion

The mechanism of formation and the self-formation of MS por-Si surface during long anodic etching in an electrolyte with an internal power source has a multistage character: 1) formation of primary porous surface, 2) the formation of a secondary the strained layer of NCs por-Si from deposited of Si adatoms; 3) formation of a netted surface texture of por-Si; 4) the formation of 3D islets NCs por-Si and self-formation of MS surface por-Si.

In the mechanism of formation and self-organization of MS por-Si very important is process pre-oxidation silicon surface during long anodic etching p-Si (100) in electrolytes with an internal current source. It is assumed that in the process of intensive surface oxidation of silicon the important role plays the singlet oxygen, which are formed in the electrolyte HF with the addition of H₂O₂ through the catalytic effect of the developed surface of por-Si.

Formation mechanism and self-organization of MS por-Si surface at long anodic etching p-Si (100) in electrolyte with internal source of current is determined by the processes of origin of islets NCs por-Si on atomic-rough surface of real monocrystals and the quantum-dimensional effects, taking place there, also as well as at the epitaxial growth of NCs-Si. In all these processes on surface of real crystal essential role play long-range forces - elastically-deformation force, defect-deformation force and capillary-fluctuation force.

Efficiency of the development of these forces in processes of self-organization of MS por-Si depends of conditions concrete experiment on the modification of surface real crystal, in which not always is revealed their quantum character.

Formation of highly ordered MS por-Si going at nanoscale level with the appearance of quantum effects, display of which depend from the specific conditions of the experiment on the surface modification. The similarly condition in this concrete experiment on formation of highly ordered MS por-Si during long anodic etching p-Si (100), is an electrolyte with an internal power source, where with the participation of the fluctuation of the electric field is established the mode of self-consistent etching.

Based on received results made conclusion about common the nature the cracks of radiation and nonradiation the origin, when in conditions soft influence possible the formation of point defects and their migration to the different drains with further of pores formation from which are formed the cracks.

Acknowledgment

I am grateful to Yu. A. Ryabikin, B. A. Rakhymetov, T. Aitmukan, K.A.Mit', M.A. Eleuov and S. Zh. Tokmoldin for help in this work. This work was supported financially by the Ministry of Science and Education of Republic of Kazakhstan.

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